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Derivation of instanton rate theory from first principles

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Derivation of instanton rate theory from first principles

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Instanton rate theory is used to study tunneling events in a wide range of systems including low-temperature chemical reactions. Despite many successful applications, the method has never been obtained from first principles, relying instead on the “Im F ” premise. In this paper, the same expression for the rate of barrier penetration at finite temperature is rederived from quantum scattering theory [W. H. Miller, S. D. Schwartz, and J. W. Tromp, *J. Chem. Phys.* **79**, 4889 (1983)] using a semiclassical Green’s function formalism. This justifies the instanton approach and provides a route to deriving the rate of other processes. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943866>]

I. INTRODUCTION

Nuclear tunneling can significantly affect chemical reactivity,^{1–3} but the most common theoretical methods for estimating reaction rates^{4–6} treat the nuclear dynamics using classical principles, which neglect these important effects. In large complex systems, quantum dynamics is far more difficult to simulate than its classical counterpart. However, using semiclassical considerations, one can describe certain quantum effects with an efficiency similar to that of a classical calculation. Here, a first-principles derivation is presented for semiclassical instanton theory which describes the rate of quantum-mechanical tunneling through an energy barrier, such as occurs in low-temperature chemical reactions.

Instanton rate theory is widely used in various scientific disciplines from subnuclear physics to cosmology.^{7–11} It is well established that the instanton describes the correct physics¹² and rates compare favorably with exact quantum calculations.^{13–15} However, despite these successes, no first-principles derivation of instanton rate theory has been presented up till now. A first-principles derivation is taken to mean one which starts from an exact expression for the rate and makes a number of well-controlled approximations. At no intermediate point should the expression evaluate to an unphysical result.

The traditional derivation of instanton theory is based on the premise that the low-temperature rate of decay of a metastable state, k , is related to the system’s free-energy, F , by $k \approx -(2/\hbar)\text{Im } F$.^{16–18} This formula is not an exact definition of the rate. In fact, it must be modified at high temperatures and its application at intermediate temperatures⁸ is understood simply as an approximate interpolation between known low and high-temperature limits.¹⁹ The imaginary part of the free-energy can only be obtained at its semiclassical limit using an analytic continuation of a divergent integral.²⁰

It is difficult to see how this concept can apply rigorously to chemical reactions, which are described by Hermitian Hamiltonians and have therefore purely real free-energies.^{21,22} Chemical reaction rates can, however, be rigorously defined using scattering boundary conditions²³ and it is not obvious how the rate defined in this way is related to the Im F approach. An alternative (and earlier) formulation of instanton theory by Miller^{12,13,24} employs the heuristic Weyl correspondence rule²⁵ in a particular transition-state theory (TST) approximation²⁴ to the rate. Such TSTs are not unique and the particular form used here is equivalent to an expression first given by Wigner.²⁶ This intermediate step is not valid at the low temperatures where the instanton is applied and can evaluate to give an unphysical negative rate.²⁷ In both this and the Im F case, however, semiclassical approximations to the expressions result in the same instanton rate,²⁸ although neither should be considered a first-principles derivation.

Recently it has become possible to evaluate these quantum rates in complex molecular systems using the ring-polymer instanton (RPI) method.²⁹ This approach locates the instanton on the full potential-energy surface by searching for stationary points of the discretized action using multidimensional optimization techniques. It has been applied successfully to many problems of interest from reactive scattering to diffusion on metal surfaces and hydrogen transfers in enzymes.^{14,15,29,30} Other related approaches are also based on Im F .^{31–35} Note that instanton theory describing tunneling splitting between degenerate minima is not discussed here as its derivation is already rigorous;^{7,8,36} the instanton referred to in this paper has sometimes been called a “bounce” to differentiate it. The RPI method also plays a significant role in explaining the success of the ring-polymer molecular dynamics (RPMD) method³⁷ for computing reaction rates in the deep-tunneling regime.^{27,29} The quantum instanton (QI) approach is also related, although its applicability is somewhat hampered by the requirement to locate two optimal dividing surfaces.^{38,39}

Here, a formalism is used based on recently obtained expressions for semiclassical approximations to the Green’s functions in the classically forbidden region.⁴⁰ The same

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approach can be used to derive a golden-rule instanton approach for nonadiabatic electron-transfer reactions,^{40,41} and thus unifies the adiabatic (where the Born-Oppenheimer approximation is valid) and nonadiabatic limits of reaction rates into one theory.

II. DERIVATION OF INSTANTON THEORY

Consider the dynamics of an adiabatic chemical reaction. The Hamiltonian is $\hat{H} = |\hat{\mathbf{p}}|^2/2m + V(\hat{\mathbf{x}})$, where $\mathbf{x} = (x_1, \dots, x_f)$ are the Cartesian coordinates of f nuclear degrees of freedom. These nuclei move on the potential-energy surface $V(\mathbf{x})$ with conjugate momenta $\mathbf{p} = (p_1, \dots, p_f)$. Without loss of generality, the degrees of freedom have been mass-weighted such that each has the same mass, m . For simplicity it will be assumed that the Hamiltonian is neither translationally nor rotationally invariant, but the following arguments can easily be generalized for this case.⁴²

An $(f-1)$ -dimensional dividing surface, defined by $\sigma(\mathbf{x}) = 0$, separates reactants, $\sigma < 0$, from products, $\sigma > 0$. The reaction probability at energy E is²³

$$P(E) = 2\hbar^2 \text{Tr} [\hat{F} \text{Im} \hat{G}(E) \hat{F} \text{Im} \hat{G}(E)], \quad (1)$$

where $\hat{G}(E) = \lim_{\eta \rightarrow 0^+} (E + i\eta - \hat{H})^{-1}$ is the Green's function. The flux from reactants to products is^{23,25}

$$\hat{F} = \frac{i}{\hbar} [\hat{H}, \theta[\sigma(\hat{\mathbf{x}})]] = \frac{\delta[\sigma(\hat{\mathbf{x}})] \hat{\mathbf{p}}_\sigma + \hat{\mathbf{p}}_\sigma^\dagger \delta[\sigma(\hat{\mathbf{x}})]}{2m}, \quad (2)$$

where $\hat{\mathbf{p}}_\sigma = \frac{\partial \sigma}{\partial \mathbf{x}} \cdot \hat{\mathbf{p}}$ and θ is the Heaviside step function. The exact reaction probability is therefore given by

$$P(E) = \frac{\hbar^2}{m^2} \iint \rho(\mathbf{x}', \mathbf{x}'') \delta[\sigma(\mathbf{x}')] \delta[\sigma(\mathbf{x}'')] d\mathbf{x}' d\mathbf{x}'', \quad (3)$$

where

$$\rho(\mathbf{x}', \mathbf{x}'') = \langle \mathbf{x}' | \hat{\mathbf{p}}_\sigma \text{Im} \hat{G}(E) | \mathbf{x}'' \rangle \langle \mathbf{x}'' | \hat{\mathbf{p}}_\sigma \text{Im} \hat{G}(E) | \mathbf{x}' \rangle + \langle \mathbf{x}' | \hat{\mathbf{p}}_\sigma \text{Im} \hat{G}(E) \hat{\mathbf{p}}_\sigma^\dagger | \mathbf{x}'' \rangle \langle \mathbf{x}'' | \text{Im} \hat{G}(E) | \mathbf{x}' \rangle. \quad (4)$$

$P(E)$ is invariant to $\sigma(\mathbf{x})$ but it is normally sensible to choose the dividing surface such that it cuts through the barrier.²³

The thermal reaction rate, k , at reciprocal temperature $\beta = 1/k_B T$ is given by

$$k Z_r = \frac{1}{2\pi\hbar} \int P(E) e^{-\beta E} dE, \quad (5)$$

where Z_r is the partition function per unit volume of the isolated reactants. Although the rate is only rigorously defined in this way for systems with scattering boundary conditions, assuming an appropriate separation of time-scales,⁴³ it can also be applied to condensed-phase reactions.

The formulation presented so far defines the quantum reaction rate but cannot be applied to complex systems due to the difficulty of obtaining the exact multidimensional Green's functions. Instead, they will be treated by the semiclassical approximation described in Ref. 40, which gives the asymptotic result in the $\hbar \rightarrow 0$ limit.⁴⁴ This is an extension of Gutzwiller's formulation⁴⁵ to the classically forbidden region where $V(\mathbf{x}'), V(\mathbf{x}'') > E$. Here the imaginary part of the semiclassical Green's functions can be written as

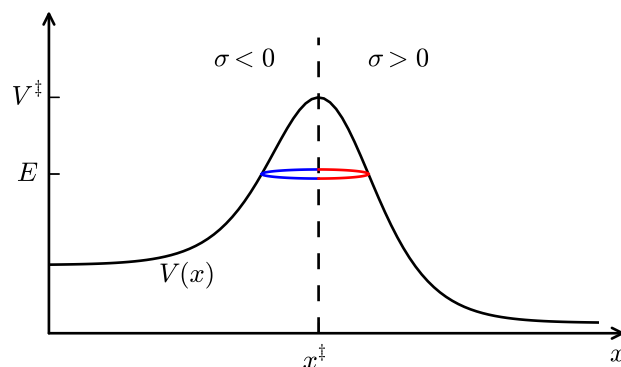


FIG. 1. Schematic showing the instanton orbit modeling tunneling through a reaction barrier of height V^\ddagger . The orbit is made up of two trajectories that both start and end at the dividing surface $\sigma = x - x^\ddagger$ (dashed line) but bounce either on the left (blue) or right (red) and contribute to Γ^- or Γ^+ , respectively.

a sum over imaginary-time classical trajectories that bounce at a point where $V(\mathbf{x}) = E$. Imaginary-time trajectories have equations of motion equivalent to Newtonian dynamics in an upside-down potential.⁴⁶ Complex-time trajectories that enter the classically allowed region can be ignored, as these add phase oscillations to the Green's functions and give a subdominant contribution to the integral in Eq. (5).⁴⁰

Only trajectories starting and ending at the dividing surface contribute to Eq. (3). For a tunneling reaction, such as that depicted in Fig. 1, where the energy is lower than the barrier height, there will be two bouncing trajectories that encounter a turning point either on the + or - side of the dividing surface, where $\pm\sigma > 0$. Those that bounce more than once can be ignored, as they have larger actions and therefore exponentially smaller contributions. The imaginary part of the Green's function is then $\langle \mathbf{x}' | \text{Im} \hat{G}(E) | \mathbf{x}'' \rangle \simeq \Gamma^- + \Gamma^+$, where the contribution from each trajectory is⁴⁰

$$\Gamma^\pm \equiv \Gamma^\pm(\mathbf{x}', \mathbf{x}'', E) = -\frac{\pi \sqrt{\bar{D}^\pm}}{(2\pi\hbar)^{(f+1)/2}} e^{-\bar{W}^\pm/\hbar}. \quad (6)$$

The abbreviated action is the following line integral along the respective classical trajectory:

$$\bar{W}^\pm \equiv \bar{W}^\pm(\mathbf{x}', \mathbf{x}'', E) = \int_{\mathbf{x}(q)=\mathbf{x}''}^{\mathbf{x}(q)=\mathbf{x}'} \bar{\mathbf{p}}(q) dq, \quad (7)$$

$$\bar{\mathbf{p}}(q) = \sqrt{2m[V(\mathbf{x}) - E]}, \quad (8)$$

and the prefactors are

$$\bar{D}^\pm = (-1)^{f+1} \begin{vmatrix} \frac{\partial^2 \bar{W}^\pm}{\partial \mathbf{x}' \partial \mathbf{x}''} & \frac{\partial^2 \bar{W}^\pm}{\partial \mathbf{x}' \partial E} \\ \frac{\partial^2 \bar{W}^\pm}{\partial E \partial \mathbf{x}''} & \frac{\partial^2 \bar{W}^\pm}{\partial E^2} \end{vmatrix} = \frac{m^2}{\bar{\mathbf{p}}(\mathbf{x}') \bar{\mathbf{p}}(\mathbf{x}'')} A^\pm, \quad (9)$$

$$A^\pm = \left| -\frac{\partial^2 \bar{W}^\pm}{\partial \mathbf{Q}' \partial \mathbf{Q}''} \right|, \quad (10)$$

where the coordinate system has been transformed from \mathbf{x} to (q, \mathbf{Q}) ,⁴⁵ defined such that q is parallel to the trajectory and equal to 0 at the dividing surface, and $\mathbf{Q} = (Q_1, \dots, Q_{f-1})$ are the perpendicular modes.⁴⁷

The reaction probability, Eq. (3), requires not only matrix elements of the Green's function but also the application of momentum operators on them. These operators can be written

in the position basis as $\hat{p}_j = -i\hbar \frac{\partial}{\partial x_j}$, such that their effect is that of differentiation of the Green's function.²³ However, because only the terms of the lowest order in \hbar are required for the semiclassical approximation, the differentiation can be applied only to the exponential. The operator thus simply multiplies the Green's function by $\pm i\bar{p}(\mathbf{x}') \frac{\partial x'_j}{\partial q'}$ (or the equivalent with double primes), which are the momentum components at the end points of the trajectory; they are imaginary and the sign depends on the direction traveled. Within the semiclassical approximation, therefore, the momentum operators act like classical variables.

Using the symmetry of $\Gamma^\pm(\mathbf{x}', \mathbf{x}'', E) = \Gamma^\pm(\mathbf{x}'', \mathbf{x}', E)$,

$$\rho(\mathbf{x}', \mathbf{x}'') \approx i^2 \left[(\bar{p}'_\sigma \Gamma^- - \bar{p}'_\sigma \Gamma^+) (\bar{p}''_\sigma \Gamma^- - \bar{p}''_\sigma \Gamma^+) + (-\bar{p}'_\sigma \Gamma^- \bar{p}''_\sigma - \bar{p}'_\sigma \Gamma^+ \bar{p}''_\sigma) (\Gamma^- + \Gamma^+) \right] \quad (11)$$

$$= 4\bar{p}'_\sigma \bar{p}''_\sigma \Gamma^+ \Gamma^-, \quad (12)$$

where $\bar{p}'_\sigma = \left| \frac{\partial \sigma}{\partial q'} \right| \bar{p}(\mathbf{x}')$ is the magnitude of the momentum normal to the dividing surface at the end point \mathbf{x}' ; the definition with double primes is equivalent. All terms cancel except the cross term with trajectories that bounces once on the left and once on the right. Unlike for the QI method,³⁸ it was not necessary to introduce a second dividing surface to ensure this outcome.⁴⁸ This is because spurious half-instantons, which cause Wigner's TST to fail at low temperature,²⁷ cannot form as trajectories contributing to $\text{Im } \hat{G}(E)$ are required to bounce.

Therefore, using $\delta[\sigma(\mathbf{x})] = \delta(q) \left| \frac{\partial \sigma}{\partial q} \right|^{-1}$, the semiclassical reaction probability is

$$P_{\text{SC}}(E) = (2\pi\hbar)^{1-f} \iiint \frac{\bar{p}(\mathbf{x}') \bar{p}(\mathbf{x}'')}{m^2} \sqrt{\bar{D}^- \bar{D}^+} e^{-\bar{W}/\hbar} \times \delta(q') \delta(q'') dq' dq'' d\mathbf{Q}' d\mathbf{Q}'', \quad (13)$$

where $\bar{W} = \bar{W}^- + \bar{W}^+$ is the total action along both trajectories. Performing the integrals over \mathbf{Q}' and \mathbf{Q}'' by the method of steepest descent (SD) gives

$$P_{\text{SC}}(E) = Z^\ddagger e^{-\bar{W}/\hbar}, \quad (14)$$

$$Z^\ddagger = \sqrt{A^- A^+} \left| \begin{array}{cc} \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}' \partial \mathbf{Q}'} & \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}' \partial \mathbf{Q}''} \\ \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}'' \partial \mathbf{Q}'} & \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}'' \partial \mathbf{Q}''} \end{array} \right|^{-\frac{1}{2}}. \quad (15)$$

All quantities are evaluated at the stationary point $\mathbf{x}' = \mathbf{x}'' = \mathbf{x}^\ddagger$ on the dividing surface where $\frac{\partial \bar{W}}{\partial \mathbf{Q}'} = \frac{\partial \bar{W}}{\partial \mathbf{Q}''} = 0$. Here the trajectories join smoothly into each other to form a continuous periodic orbit, known as an instanton.

In the one-dimensional case, the formula reduces to $P_{\text{SC}}(E) = e^{-W/\hbar}$, which is the well-known WKB result.⁴⁹ The supplementary material⁵⁰ outlines a proof that Z^\ddagger is a particular generalization of the partition function of the instanton such that $P_{\text{SC}}(E)$ is equivalent to an expression given by Miller in Ref. 24. The final result is therefore independent of the choice of dividing surface and requires only that the instanton orbit intersects the surface at some point. The instanton could be thought of as defining a dividing region around the barrier.⁵¹

Note that the short-time approximation inherent in the semiclassical Green's functions is not necessarily valid when computing microcanonical rates as it cannot describe nuclear

coherences leading, for instance, to discrete densities of states in a reactant well. The approximation is however asymptotically correct when energy is integrated over a smooth distribution such as the thermal distribution considered next.

The semiclassical thermal rate is found by evaluating the integral in Eq. (5) by steepest-descent²⁴ to give

$$k_{\text{SC}} Z_r = (2\pi\hbar)^{-\frac{1}{2}} P_{\text{SC}}(E) \left(\frac{d^2 \bar{W}}{dE^2} \right)^{-\frac{1}{2}} e^{-\beta E}, \quad (16)$$

where E solves $\frac{\partial \bar{W}}{\partial E} = -\beta\hbar$. As the imaginary time taken by each trajectory is $\tau^\pm = -\frac{\partial \bar{W}^\pm}{\partial E}$, the total time is $\beta\hbar$. The total derivatives are found using $q' = q'' = 0$ and recognizing that \mathbf{Q}' and \mathbf{Q}'' are functions of E .

Assuming the barrier approximates the parabola $V(x) = -m\omega^2 x^2$ in one degree of freedom near its top, it cannot support periods less than $2\pi/\omega$. The instanton approach is thus only defined for low temperatures when the periodic orbit exists. Extensions of the approach to treat higher temperatures, and involving terms with higher orders of \hbar , have been suggested.^{12,34,52}

The result can be converted to the Lagrangian formulation using a Legendre transformation similar to that in Ref. 40. This is based on the full action,

$$\bar{S}^\pm \equiv \bar{S}^\pm(\mathbf{x}', \mathbf{x}'', \tau^\pm) = \bar{W}^\pm(\mathbf{x}', \mathbf{x}'', E) + E\tau^\pm, \quad (17)$$

where E is defined such that the trajectories from \mathbf{x}'' to \mathbf{x}' are completed in imaginary time τ^\pm . Using $\bar{S} = \bar{S}^- + \bar{S}^+$, and $\frac{d^2 \bar{W}}{dE^2} = -\hbar \frac{d\beta}{dE} = -\hbar \left(\frac{dE}{d\beta} \right)^{-1}$, Eq. (16) becomes

$$k_{\text{SC}} Z_r = (2\pi\hbar^2)^{-\frac{1}{2}} Z^\ddagger \left(-\frac{dE}{d\beta} \right)^{\frac{1}{2}} e^{-\bar{S}/\hbar}, \quad (18)$$

which was also obtained by Miller,²⁴ or equivalently

$$k_{\text{SC}} Z_r = (2\pi\hbar)^{-\frac{1}{2}} \sqrt{\frac{\Sigma^- \Sigma^+}{-\Sigma}} e^{-\bar{S}/\hbar}, \quad (19)$$

where $\tau = \tau^+ = \beta\hbar - \tau^-$ and, from Ref. 40,

$$\Sigma^\pm = \begin{vmatrix} \frac{\partial^2 \bar{S}^\pm}{\partial \mathbf{Q}' \partial \mathbf{Q}''} & \frac{\partial^2 \bar{S}^\pm}{\partial \mathbf{Q}' \partial \tau^\pm} \\ \frac{\partial^2 \bar{S}^\pm}{\partial \tau^\pm \partial \mathbf{Q}''} & \frac{\partial^2 \bar{S}^\pm}{\partial \tau^\pm \partial \tau^\pm} \end{vmatrix} = (-1)^{f-1} A^\pm \frac{\partial^2 \bar{S}^\pm}{\partial \tau^{\pm 2}},$$

$$\Sigma = \frac{d^2 \bar{S}}{d\tau^2} \begin{vmatrix} \frac{\partial^2 \bar{S}}{\partial \mathbf{Q}' \partial \mathbf{Q}'} & \frac{\partial^2 \bar{S}}{\partial \mathbf{Q}' \partial \mathbf{Q}''} \\ \frac{\partial^2 \bar{S}}{\partial \mathbf{Q}'' \partial \mathbf{Q}'} & \frac{\partial^2 \bar{S}}{\partial \mathbf{Q}'' \partial \mathbf{Q}''} \end{vmatrix}$$

$$= \frac{d^2 \bar{W}}{dE^2} \begin{vmatrix} \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}' \partial \mathbf{Q}'} & \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}' \partial \mathbf{Q}''} \\ \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}'' \partial \mathbf{Q}'} & \frac{\partial^2 \bar{W}}{\partial \mathbf{Q}'' \partial \mathbf{Q}''} \end{vmatrix}.$$

Equation (19) can be evaluated numerically using the RPI algorithms to obtain the instanton and its action²⁹ and derivatives.⁴¹ This may lead to a better strategy for evaluating instanton rates in multidimensional complex systems than the standard RPI approach, Eq. (22), for which an $N_f \times N_f$ matrix must be diagonalized. Other approaches for locating the instanton orbit are also naturally suggested such as using

the Hamilton-Jacobi formulation with end points constrained to bounce⁴¹ or modifications of the nudged-elastic-band method.^{53,54}

III. EQUIVALENCE TO IMF INSTANTON

Following Ref. 28, it can be shown that the semiclassical result Eq. (19) is equivalent to the RPI rate in the $N \rightarrow \infty$ limit²⁹ and hence to the standard instanton rate theories.^{8,18,19} These are based on the Im F premise,^{12,16} $kZ_\tau \approx \frac{2}{\beta\hbar} \text{Im } Z(\beta)$ and the partition function can be evaluated in ring-polymer form as

$$Z(\beta) \equiv e^{-\beta F} = \Lambda^{-Nf} \int \dots \int e^{-\beta_N U_N(\mathbf{x})} d\mathbf{x}. \quad (20)$$

Here, the integration is over N ring-polymer beads $\mathbf{x} = \{\mathbf{x}_1, \dots, \mathbf{x}_N\}$; $\beta_N = \beta/N$, $\Lambda = \sqrt{2\pi\beta_N\hbar^2/m}$ and the ring-polymer potential is

$$U_N(\mathbf{x}) = \sum_{i=1}^N \frac{m}{2\beta_N^2\hbar^2} |\mathbf{x}_i - \mathbf{x}_{i+1}|^2 + V(\mathbf{x}_i), \quad (21)$$

where the indices are cyclic such that $\mathbf{x}_0 \equiv \mathbf{x}_N$. This is a discretization of the path-integral approach to quantum statistics,⁵⁵ and in the $N \rightarrow \infty$ limit, gives the partition function exactly.

The imaginary part of the partition function is, however, not well defined and it can only be obtained using analytic continuation. In practice, one takes a steepest-descent integral about the saddle point of $U_N(\mathbf{x})$,^{28,29} but reverses the sign of the negative eigenvalue and multiplies the integral by a half.^{7,20} There is also a zero-eigenvalue mode that is integrated out analytically. This procedure gives the RPI rate,²⁹

$$k_{\text{RPI}}Z_\tau = \frac{\Lambda^{-1}}{\beta_N\hbar} \sqrt{\sum_{i=1}^N |\mathbf{x}_i - \mathbf{x}_{i-1}|^2} \prod_k' \left| \frac{1}{\beta_N\hbar\eta_k} \right| e^{-\beta_N U_N}, \quad (22)$$

where $m\eta_k^2$ are the Nf eigenvalues of the ring-polymer Hessian $\nabla^2 U_N$; the prime indicates that the mode for which $\eta_k = 0$ is not included in the product.

Although Eq. (22) is the form employed in RPI calculations, equivalent expressions are found by taking the integrals in a different order.²⁸ Steepest-descent integration of Eq. (20) over all beads but the two on the dividing surface gives

$$Z(\beta) \approx 2\Lambda^{-2f} \iint \frac{1}{\sqrt{|\mathbf{J}^-||\mathbf{J}^+|}} e^{-\tilde{S}(\mathbf{x}',\mathbf{x}'')/\hbar} d\mathbf{x}'d\mathbf{x}'', \quad (23)$$

where the factor of 2 appears because of the degeneracy of the ring-polymer space, as the order of the beads along the orbit can be reversed. The square Hessian matrices \mathbf{J}^\pm are defined as in Ref. 41 from second-derivatives of $U_N(\mathbf{x})$ with respect to the beads on the $\pm\sigma > 0$ side of the dividing surface. A further coordinate transformation, $d\mathbf{x}' = d\mathbf{q}'d\mathbf{Q}' = \dot{\mathbf{q}}'d\tau'd\mathbf{Q}'$, describes the position along the trajectory using imaginary time. The instanton orbit folds back on itself so τ' has a range of $\frac{1}{2}\beta\hbar$ and $\dot{\mathbf{q}}' = \left| \frac{d\mathbf{q}'}{d\tau'} \right|$, which could be estimated using $|\mathbf{x}_{i+1} - \mathbf{x}_i|/\beta_N\hbar$ and the appropriate index i . The equivalent holds for double primes. Due to the cyclic permutational

symmetry around the ring polymer,²⁹ the integral over one time variable is simple giving

$$Z(\beta) \approx 2\Lambda^{-2f} \iiint \frac{\frac{1}{2}\beta\hbar\dot{\mathbf{q}}'\dot{\mathbf{q}}''}{\sqrt{|\mathbf{J}^-||\mathbf{J}^+|}} e^{-\tilde{S}/\hbar} d\tau d\mathbf{Q}'d\mathbf{Q}'', \quad (24)$$

whereas the second over the remaining τ is completed, according to the usual Im F procedure, using analytic continuation of steepest-descent over an imaginary mode and multiplying by a factor of half,

$$\text{Im } Z(\beta) \approx \frac{\sqrt{2\pi\hbar}}{\Lambda^{2f}} \iint \frac{\frac{1}{2}\beta\hbar\dot{\mathbf{q}}'\dot{\mathbf{q}}''}{\sqrt{|\mathbf{J}^-||\mathbf{J}^+|}} \left| \frac{d^2\tilde{S}}{d\tau^2} \right|^{-\frac{1}{2}} e^{-\tilde{S}/\hbar} d\mathbf{Q}'d\mathbf{Q}''.$$

The remaining integrals over the perpendicular directions are performed using steepest-descent to give

$$k_{\text{RPI}}Z_\tau = (2\pi\hbar)^{-\frac{1}{2}} \left(\frac{m}{\beta_N\hbar} \right)^f \frac{\dot{\mathbf{q}}'^2 |\Sigma|^{-1/2}}{\sqrt{|\mathbf{J}^-||\mathbf{J}^+|}} e^{-\tilde{S}/\hbar}, \quad (25)$$

where at the stationary point $\dot{\mathbf{q}}' = \dot{\mathbf{q}}'' = \dot{\mathbf{q}}$. In the $N \rightarrow \infty$ limit, this formulation is equivalent to all Im F instanton rates^{8,14,15,18,19,28-30} including Eq. (22).

It is now a simple matter to show that Eq. (25) is equivalent to the first-principles rate derived above from the semiclassical Green's functions, i.e., $k_{\text{SC}} = \lim_{N \rightarrow \infty} k_{\text{RPI}}$. From Eq. (9), and using a number of relations stated in Refs. 40 and 41, the necessary equations are

$$(-1)^{f+1} \Sigma^\pm / \dot{\mathbf{q}}^2 = \left| -\frac{\partial^2 \tilde{S}^\pm}{\partial \mathbf{x}' \partial \mathbf{x}''} \right| = \left(\frac{m}{\beta_N\hbar} \right)^f |\mathbf{J}^\pm|^{-1}. \quad (26)$$

IV. CONCLUSIONS

In summary, the instanton method for computing the rate of tunneling through a barrier on a Born-Oppenheimer potential-energy surface has been rederived from a semiclassical limit of exact scattering theory.²³ In contrast to this, previous derivations have employed semiclassical approximations to either the Im F premise¹⁹ or a transition-state theory approximation.²⁴ The final form found here is, however, equivalent to the usual instanton expression, although the derivation is more rigorous. The semiclassical instanton appears from the reaction probability at a given energy before temperature has been introduced. This is in contrast with other path-integral rate theories based on the Boltzmann operator.^{21,27,31-33,37,56} Real-time dynamical information does not contribute, as is appropriate for a complex dissipative system where nuclear coherence is washed out. However, unlike TST or QI methods,^{21,27,31-33,38,39,56} the instanton rate remains independent of the dividing surface so long as the instanton orbit intersects it. In light of this new derivation, applications of instanton methods can be better understood and the development of new RPMD and QI approaches advanced. Generalizations of the new derivation provide a new route to solving novel problems such as nonadiabatic reaction rates.⁴⁰

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